Actinide Foil Production for MPACT Research

Fuel Cycle R&D

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Abstract

Sensitive fast-neutron detectors are required for use in lead slowing down spectrometry (LSDS), an active interrogation technique for used nuclear fuel assay for Materials Protection, Accounting, and Controls Technologies (MPACT). During the past several years UNLV sponsored a research project at RPI to investigate LSDS; began development of fission chamber detectors for use in LSDS experiments in collaboration with INL, LANL, and Oregon State U.; and participated in a LSDS experiment at LANL. In the LSDS technique, research has demonstrated that these fission chamber detectors must be sensitive to fission-energy neutrons but insensitive to thermal-energy neutrons. Because most systems are highly sensitive to large thermal neutron populations due to the well-known large thermal cross section of ^{235}U, even a miniscule amount of this isotope in a fission chamber will overwhelm the small population of higher-energy neutrons. Thus, fast-fission chamber detectors must be fabricated with highly depleted uranium (DU) or ultra-pure thorium (Th), which is about half as efficient as DU. Previous research conducted at RPI demonstrated that the required purity of DU for assay of used nuclear fuel using LSDS is less than 4 ppm ^{235}U, material that until recently was not available in the U.S.

In 2009 the PI purchased 3 grams of ultra-depleted uranium (uDU, 99.99998% ^{238}U with just 0.2 ± 0.1 ppm ^{235}U) from VNIIEF in Sarov, Russia. We received the material in the form of U_3O_8 powder in August of 2009, and verified its purity and depletion in a FY10 MPACT collaboration project. In addition, chemical processing for use in FC R&D was initiated, fission chamber detectors and a scanning alpha-particle spectrometer were developed, and foils were used in a preliminary LSDS experiment at a LANL/LANSCE in Sept. of 2010. The as-received U_3O_8 powder must be chemically processed to convert it to another chemical form while maintaining its purity, which then must be used to electro-deposit U or UO_2 in extremely thin layers (1 to 2 mg/cm^2) on various media such as films, foils, or discs. After many months of investigation and trials in FY10 and 11, UNLV researchers developed a new method to produce pure UO_2 deposits on foils using a unique approach, which has never been demonstrated, that involves dissolution of U_3O_8 directly into room-temperature ionic liquid (RTIL) followed by electro-deposition from the RTIL-uDU solution (Th deposition from RTIL had been previously demonstrated). The high-purity dissolution of the U_3O_8 permits the use of RTIL solutions for deposition of U on metal foils in layers without introducing contamination. In FY10 and early FY11 a natural U surrogate for the uDU was used to investigate this and other techniques.

In this research project UNLV researchers attempted to further develop the capability to deposit directly from RTIL to produce uDU and Th foils devoid of possible contaminants. We intended that after these layers were deposited, they would be examined for purity and uniformity. UNLV did not complete the development and demonstration of the RTIL technology/methodology to

prepare uDU and Th samples for use in constructing fast-neutron detectors because of a radiation contamination issue that allowed less than the full year of research. This report includes the progress achieved to date, but does not report full success in creating usable uDU and Th foils for use in MPACT LSDS research projects.

Introduction

Several techniques have been studied and/or proposed for Materials Protection, Accounting, and Controls Technologies (MPACT) that require the use of sensitive neutron detectors in active and passive interrogation techniques, such as lead slowing down spectrometer (LSDS) experiments at a collaborating university[1] and a national laboratory[2, 3] and the Passive Neutron Albedo Reactivity (PNAR)[4] technique being investigated at a national laboratory and the Lead University. One requirement for some of these projects is an array of sensitive fast- neutron fission detectors. During the past several years the Lead University sponsored a research project at a collaborating university to investigate LSDS[5,6]; began development of fission chamber detectors for use in LSDS experiments in collaboration with two national laboratories and a collaborating university[7]; and worked with a safeguards group at a national laboratory to study the feasibility of PNAR. Both of these studies have been based on the use of fission chamber detectors. In some applications, such as PNAR, fission chamber detectors (FCD) are utilized that contain highly enriched uranium (HEU). However, in other applications, such as the LSDS for assay of used fuel, the FCDs must be sensitive to fission-energy neutrons but insensitive to thermal-energy neutrons to reduce background count rates. Because of high neutron absorption sensitivity to large thermal neutron populations in most systems due to the well-known large thermal cross section of ^{235}U, even a miniscule amount of this isotope in a fission chamber will overwhelm the small population of higher-energy neutrons. Thus, fast-fission chamber detectors must be fabricated with highly depleted uranium (DU) or ultra-pure thorium (Th), which is about half as efficient as DU. Previous research conducted at a collaborating university has demonstrated that the required purity of DU for assay of used nuclear fuel using LSDS is less than 4 ppm ^{235}U, which was not available in the U.S. prior to the initiation of this research at the Lead University.

To overcome this deficiency and to advance the technology of LSDS for assaying used nuclear fuel, in 2009 the Lead University purchased 3 grams of ultra-depleted uranium (uDU) from VNIIEF in Sarov, Russia (a quantity sufficient to fabricate many fission chamber detectors such as that illustrated in Figures 1 and 2). The material was certified to be 99.99998% ^{238}U with just 0.2 ± 0.1 ppm ^{235}U and with less than 0.01 ppm ^{234}U and ^{236}U. Based on discussions with several national laboratory personnel, it is believed to be the highest purity uranium to ever exist in the U.S. in significant quantity. We received the material in the form of U_3O_8 powder in August of 2009, and verified its purity and depletion in a FY10 MPACT collaboration project. In addition, chemical processing for use in FC R&D was initiated, fission chamber detectors and a scanning alpha-particle spectrometer were developed, and foils were used in a preliminary LSDS experiment at a national laboratory in Sept. of 2010.[7]

Because the as-received U_3O_8 powder is not useful for fission detectors, it must be chemically processed to convert it to another chemical form while maintaining its purity, which then must be used to electro-deposit U or UO_2 in extremely thin layers (1 to 2 mg/cm^2) on various media such as films, foils, or discs. The scientific literature is very limited on these methods,[8,9] and the "art" of working with actinides to produce pure samples and pure deposits requires expanded efforts.[10]

After many months of investigation and trials in FY10, the Lead University researchers developed a new method to produce pure UO_2 deposits on foils using a unique approach, which has never been demonstrated, that involves dissolution of U_3O_8 directly into room-temperature ionic liquid (RTIL) followed by electro-deposition from the RTIL-uDU solution (Th deposition from RTIL had been previously demonstrated). The high-purity dissolution of the U_3O_8 permits the use of RTIL solutions for deposition of U on metal foils in layers without introducing contamination. Thus, in this project we were to deposit directly from RTIL to produce uDU foils devoid of possible contaminants. After these layers were deposited, we intended to examine them for purity and uniformity of deposition density. From FY10 through the current NEUP project a surrogate for the uDU was used to investigate this and other techniques.

The purpose of the research proposed for this NEUP project was to complete the development and demonstration of the RTIL technology/methodology to prepare uDU and Th samples for use in constructing fast-neutron detectors. The PI and co-PI of the Lead University consulted with national laboratories and other academia in the development and demonstration of said technology as well as their use in fission chamber detectors. The report begins with a discussion of the three tasks contained within the NEUP project, including their status and concerns or issues. We then list publications and presentations that were produced during the NEUP project. We then present a more detailed description of the radiochemistry techniques and accomplishments of this project as reported by our GRA electrochemist.

Task 1: UNLV Radiochemistry personnel will advance the technology to dissolve ultra-depleted U_3O_8 in RTIL for use in electrodeposition while maintaining purity and preventing uranium contamination.

Status: The graduate researcher was able to develop a method to directly dissolve uranium oxide as U_3O_8 into the RTIL, n-trimethyl-n-butylammonium bis(trifluoromethanesulfonyl)imide ([Me$_3$NBu][TFSI]), using an oxidizing gas and the protic form of the anion (HTFSI). The soluble species in solution was confirmed through UV-Vis and extended X-ray absorption fine structure (EXAFS) to be uranyl (UO_2^{2+}). It was observed that the factors of water content and amount of HTFSI assist with the dissolution process. However, a significant amount of water could pose limitations on the ability of electrodeposition. Therefore, fundamental studies of [Me$_3$NBu][TFSI] determined that the ultimate capacity for water in this "hydrophobic" ionic liquid is approximate 1.4 wt. %. To reduce and manage water content after dissolution, methods to dry the RTIL such as purging with an inert gas and molecular sieves were found to be effective and convenient.

In the case of thorium, the most reliable method for introduction was the synthesis of a Th-TFSI salt from aqueous conditions. These synthesized products of Th(TFSI)$_4$ were then dissolved into the RTIL.

Issues/Concerns: There were initially inconsistencies with the dissolution of the U_3O_8 into the ionic liquid. It has subsequently been determined that this was likely due to a varying amount of water in solution. A certain percentage of water in the ionic liquid helps to initially complete dissolution. After dissolution, depending on the water content, the ionic liquid may require purging or molecular sieves to reduce the water content before electrodeposition is attempted.

Task 2: UNLV personnel will complete the development of technology to deposit uDU and Th on small to large disks, foils, membranes, and/or films.

Status: The fundamental electrochemistry of a representative solution containing U from the direct dissolution of U_3O_8 was investigated in hopes of better understanding the chemistry and potentials that could be exploited for reduction of U species from solution. The electrochemical study seems to provide evidence of a step-wise reduction in which the pentavalent species of uranium can be observed (not typically stable in aqueous environments). The cyclic voltammetry suggests the electrochemical reduction proceeds through a mechanism of U(VI) → U(V) → U(IV) → $UO_{2\,(s)}$ under the conditions currently explored in the ionic liquid.

Thus far, deposit densities above 0.6 mg/cm^2 were not achieved using the electrodeposition cell and stainless steel. However, a smaller piece of Au foil that was used as a working electrode in a traditional 3-electrode cell set-up with the same solution previously deposited a uranium oxide which was 36 mg/cm^2 (0.74 cm^2 deposit area). This suggests another factor that has been limiting the deposit density is the size of the electrodepostion cell and the ability for the potentiostats available to the researcher to apply enough of a driving force over that area to acquire the deposit. A smaller deposit area can correlate with thicker deposits as the current density is able to be comparatively higher. This prompted a new Teflon electrodeposition cell to be manufactured in which the diameter of the deposition chamber was reduced to a diameter of 1.905 cm or a deposit area of 2.8 cm^2. As the investigation of Th in the ionic liquid was began later, only a few electrodeposition attempts were able to be completed. The results of the attempts at electrodeposition yielded no significant deposits however.

Issues/Concerns: The limits of the available potentiostat, size of initial electrodeposition cell area, and varying amounts of water in the ionic liquid solutions are believed to have contributed to deposits that were less than the desired 1 mg/cm^2. Some of these factors were being managed such as using purging and molecular sieves to reduce water content and Karl Fischer titration to quantify water content before electrodeposition. Also, the smaller electrodeposition cell was manufactured but was not able to be tested out due to unforeseen circumstances preventing the graduate student from being able to work on the project. If this had not occurred, it is possible the electrodeposition technique and smaller cell could have provided deposits able to be analyzed. As a result, the uDU was not used as there was limited material and was only planned for use once the entire process was found to be functional producing deposits on the order of the desired 1 mg/cm^2.

Task 3: UNLV personnel will quantify the mass of uDU and Th deposited and will confirm the uniformity and purity of the deposition via mass spectroscopic and other methods.

Status: Undergraduate Research Assistant Stephanie Chagin is working on modifications to a Scanning Alpha-Particle Spectrometer (SAPS) to convert it from a student design project prototype to a production system. This will involve acquisition of a digital control system and physical modifications to fit the SAPS in a vacuum chamber.

Publications and Presentations

Denis Beller, David Hatchett, John Kinyanjui, Janelle Droessler, and Stephanie Chagin, "Final Report for PNNL-UNLV LSDS MPACT Project, PNNL Subcontract No. 146298," UNLV project report, 22 pp., January 14, 2012.

Denis Beller, Janelle Droessler, David Hatchett, and Ken Czerwinski, "Update on ultra-Depleted Uranium (uDU)-based Fast Fission Detector," oral presentation, US DOE Material Protection, Control, and Accounting Technologies (MPACT) Working Group Meeting , Savannah River National Laboratory, Georgia, March 14, 2012.

Janelle Droessler, David Hatchett, Denis Beller, and Ken Czerwinski, "The Direct Dissolution and Electrochemical Study of Cerium in Ionic Liquid," oral presentationby Janelle Droesslerat the 2012 Student Conference of the American Nuclear Society, April 13, 2012. (First Place Award in the Radiochemistry Division of the Conference)

Janelle Droessler, Denis Beller, David Hatchett, and Ken Czerwinski, "The Direct Dissolution and Electrochemical Study of U_3O_8 in Ionic Liquid," presented by Janelle Droessler at the 2012 Annual Meeting of the American Nuclear Society, Chicago, IL, June 25, 2012.

Janelle Droessler, Denis Beller, David Hatchett, and Ken Czerwinski, "The Direct Dissolution and Electrochemical Study of U_3O_8 in Ionic Liquid," *Transactions of the American Nuclear Society, Vol. 106*, Chicago, Illinois, June 24–28, 2012, pp 167-169.

"The Direct Dissolution and Electrochemical Study of Uranium Oxide in Ionic Liquid," Janelle Droessler, Denis Beller, David Hatchett, and Ken Czerwinski, poster presentation by Janelle Droessler at the Plutonium Futures 2012 conference, University of Cambridge, UK, July 15-20, 2012.

Janelle Droessler, John Kinyanjui, David Hatchett, Denis Beller, and Ken Czerwinski' "The Direct Dissolution and Electrochemical Study of Uranium Oxide in Ionic Liquids," poster presentation at the Nuclear Science and Security Consortium Meeting, U.C. Berkeley, August 14, 2012.

Summary of Radiochemistry Work on the Direct Dissolution into RTIL and Electrodeposition of Targets/foils.
Janelle Droessler, UNLV

Introduction

The reprocessing of used nuclear fuel, recovery of useful materials[11, 12, 13] and the removal/storage of high activity fission waste have largely shaped the electrochemical research associated with f-elements in aqueous solutions.[14] These processes are directly influenced by the oxidation states of the actinide and lanthanide species in aqueous solution, and the research is important in the management of nuclear waste for reuse and non-proliferation.[15] Exploiting f-element redox chemistry is centrally important in the applications mentioned. Although, the use of ionic liquids as a separation media is a relatively new, it is based on the fundamental approaches currently used in aqueous separations and molten salt reprocessing.
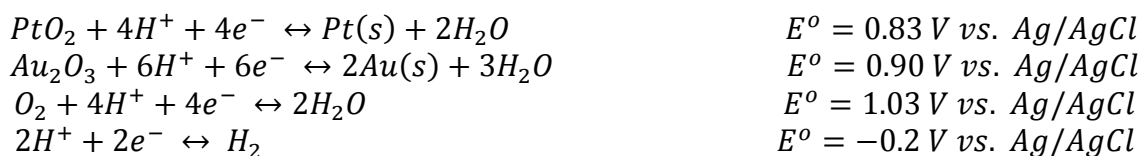
Alternative methods to the well established PUREX (Plutonium-Uranium Extraction)[616,717,818,919] have been developed that rely on treating irradiated nuclear fuels in molten salt (450 – 500 ºC) using electrochemical methods. [2010] The recovery of useable actinides and isolation of fission product is achieved through the anodic dissolution of the fuel followed by recovery of relatively pure uranium at a solid cathode. Plutonium is not isolated into a separate waste stream minimizing possible proliferation issues associated with PUREX. Molten salt methods have two main advantages including reduction of the waste volume for storage and the isolation of long-lived species that can be transmuted to more short-lived nuclides. [2111] Electrochemical control of the oxidation state of f-elements in both systems is preferred over chemical methods because the production of additional waste and increased cost is minimized. [2212] However, there are disadvantages associated with the molten salt system. The use of molten salt requires a specialized cell that is corrosion resistant in the media at elevated temperatures. In addition, special electrodes are required for the dissolution of the fuel and recovery. Finally, caustic side reactions associated with the molten salt can be problematic at elevated temperatures.

Controlled oxidation and reduction of f-elements at Hg electrodes can be accomplished in aqueous solution without elevated temperatures or specialized electrochemical cells. The Hg working electrode is the key because it forms a stable amalgam with actinide and lanthanide ions and metals. The Hg electrode provides more thermodynamically favorable reduction, while also minimizing competing side reactions such as hydrogen evolution. [2313] The thermodynamic potentials have been established for the amalgamation of both lanthanide and actinides species from aqueous solutions at Hg electrodes. [24, 25, 26, 27] In addition, the method has been used to stabilize the oxidation state of the f-element species in aqueous solutions. Finally, the electrochemical potentials and related parameters associated with the potential dependent separation of actinides and lanthanides from aqueous solution at Hg electrodes has been explored. [28, 29] These studies provide the experimental methodology and data for the possible recovery and separation of actinide and lanthanide species using polarographic methods. However, the use of Hg metal electrodes in electrochemical processes is not ideal and toxicity issues associated with the metal working electrode remain a significant drawback to its use.

In contrast to the Hg electrode, the measurement of the oxidation/reduction processes of f-elements at common electrodes including Au, Pt, and glassy carbon (GC) in aqueous solution is

difficult. The measurements are complicated by side reactions that occur at potentials that preclude the analysis electropositive lanthanide and actinides in aqueous solutions. The potential windows afforded by common electrodes in aqueous solution are constrained by water oxidation or metal oxide formation at positive potentials and by hydrogen evolution at negative potentials. The electrochemical window that can be utilized in aqueous solution depends on the electrode composition and the potentials for the side reactions is 1.3 V to 2.5 V based on the reactions provided (Equation set 1) [30, 31, 32]. Essentially, the potential window to systematically examine the thermodynamic electrochemical properties of f-elements is prohibitive in aqueous solutions due to the negative potential limit associated with the hydrogen evolution reaction.

Equation set 1

$$PtO_2 + 4H^+ + 4e^- \leftrightarrow Pt(s) + 2H_2O \qquad E^o = 0.83\ V\ vs.\ Ag/AgCl$$
$$Au_2O_3 + 6H^+ + 6e^- \leftrightarrow 2Au(s) + 3H_2O \qquad E^o = 0.90\ V\ vs.\ Ag/AgCl$$
$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \qquad E^o = 1.03\ V\ vs.\ Ag/AgCl$$
$$2H^+ + 2e^- \leftrightarrow H_2 \qquad E^o = -0.2\ V\ vs.\ Ag/AgCl$$

The disadvantages associated with the previous methods can be minimized using non-aqueous ionic liquid solutions. Ionic liquids (ILs) are chemically stable purely ionic solutions at room temperature and they are composed of cation/anion pairs that can be exploited to provide a wide range of tunable physical and chemical properties. [33, 34] Ionic liquids also provide unique solution environments for electrochemical measurements because traditional side-reactions associated with common working electrodes in aqueous solution are eliminated, thereby providing large potential windows (up to 6 V) allowing sufficiently negative potentials for electrodeposition (Figure 1). Essentially, these systems provide similar electrochemical characteristics as molten salts without the use of harsh temperature regimes reducing emission of possible toxic species and high operating costs. [35, 36, 37]
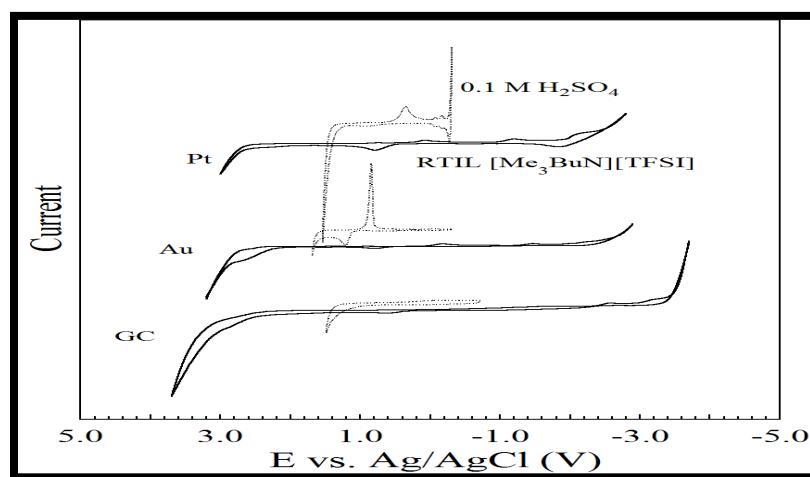

Figure 1. Electrochemistry of GC, Au, and Pt electrodes in [Me₃NBu][TFSI] (solid line) and 0.1M H₂SO₄ (dashed line)

Common cations used to prepare IL solutions include imidazolium, pyridinium, ammonium, phosphonium, and sulfonium ions paired with a variety of anions including halides, BF_4^-,

CF$_3$CF$_2$CF$_2$CO$_2^-$, N(CN)$_2^-$, and N(SO$_2$CF$_3$)$_2^-$ [TFSI] to name a few. [38] The choice of cation/anion pair is important because the electrochemical window for the solutions is based on the reduction of the cation and oxidation of the anion at the electrode surface. The potentials for cation reduction and anion oxidation in IL solutions typically occur at more positive and negative potentials which expand the potential window relative to water oxidation and hydrogen evolution. The potential window for IL is well above the maximum 2.3 V range obtained for aqueous solutions. Potential windows for ILs have been measured and typically range from approximately 4.5 to 6 V, depending on the cation/anion pair and the working electrode utilized in the experiment. [39, 40] For example, the potential windows associated with GC, Pt, and Au working electrodes in ionic liquid used in the course of these studies, trimethyl-n-butylammonium bis(trifluoromethanesulfonyl)imide ([Me$_3$BuN][TFSI], Figure 2) provides an absolute potential window of approximately 4.5 V for Pt, 5.0 V for Au, and 6.0 V for GC,
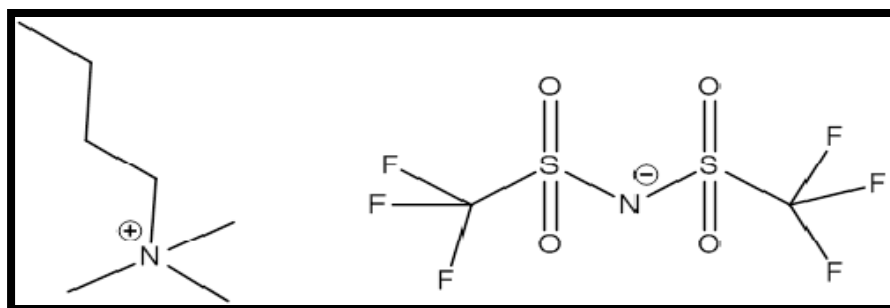
respectively. [41, 42]

Figure 2. The form of the cation/anion pair in the chosen RTIL trimethyl-n-butylammonium bis(trifluoromethanesulfonyl)imide ([Me$_3$BuN][TFSI])

The few research groups that are working in the area of f-elements in RTILs, the method of introduction is first synthesis of the complex with the common anion in aqueous solution and then dissolution of the f-element/TFSI complex into the RTIL. These complexes are often hydrated, however, so a method of direct dissolution was chosen for investigation. The fact that the method of introduction is a direct dissolution, which is not currently noted in the literature, required trial and error investigation and is still an area of the research to discover the components and mechanism of the direct dissolution.

Experimental

a. Karl-Fischer analysis of [Me$_3$NBu][TFSI]
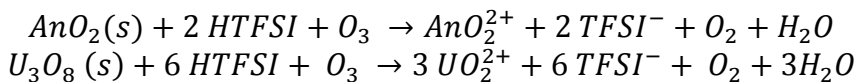
The RTIL used, trimethyl-n-butylmethylammonium bis(trifluoromethanesulfonyl)imide, [Me$_3$BuN][TFSI], was obtained from Solvionic in argon sealed 500g canisters. While the hydrophobic RTIL [Me$_3$NBu][TFSI] has relatively low water content, it is not completely free of water. In order to quantify the water content of the [Me$_3$NBu][TFSI] a Karl-Fischer Titrator (Mettler-Toledo Model DL32) was used along with HYDRANAL Coulomat CG and HYDRANAL Coulomat A reagents. The procedure included first testing the accuracy and precision with a HYDRANAL 0.1% water standard (independently tested to contain 0.1011% H$_2$O) in triplicate. Then, for each sample, triplicates were analyzed.

b. Preparation of U_3O_8

The U_3O_8 was prepared from uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$) by precipitation with concentrated ammonium hydroxide. The resulting uranium hydroxide was collected by centrifugation and the supernatant was removed. The uranium hydroxide was dried in an oven at 200°C for at least 24 hours. The product was then thermally treated in a tube furnace under air at 800°C for 6 hours. The product was analyzed and confirmed as U_3O_8 by powder X-ray diffraction. XRD patterns were obtained on a Phillips Panalytical X'Pert Pro, Cu Kα target with a Ni filter and an X'elerator multiple Si-strip solid-state detector. The XRD patterns were quantified by Reitveld analysis using TOPAS 3.0 software.

c. Direct dissolution of U_3O_8 into [Me₃NBu][TFSI]

Development of the procedure for direct dissolution of U_3O_8 into [Me₃NBu][TFSI] using the protonated form of the anion (HTFSI) was the first area of research. The original dissolution solution was 45 mg U_3O_8 (nat) with 3.27 M HTFSI in [Me₃NBu][TFSI]. The sample was stirred and purged with argon for weeks with no apparent change. Once the idea of bubbling with ozone was set up and implemented, the solid dissolved within 24 hours. Subsequent dissolutions followed a similar procedure in regards to being assisted with ozone. The ozone was from an ozone generator with breathing grade air feed gas (18-20% O_2) which resulted in 1-2 wt % ozone that was bubbled through the sample solutions. All studies were performed at room temperature (~24°C). The dissolution of actinide oxides such as AnO_2 and U_3O_8 can be explored by the following proposed reactions:

$$AnO_2(s) + 2\ HTFSI + O_3 \rightarrow AnO_2^{2+} + 2\ TFSI^- + O_2 + H_2O$$
$$U_3O_8\ (s) + 6\ HTFSI + O_3 \rightarrow 3\ UO_2^{2+} + 6\ TFSI^- + O_2 + 3H_2O$$

Over time other dissolutions of U_3O_8 were examined including a sample which pre-conditioned the RTIL before adding the U_3O_8 and then underwent sequential ~50 mg U_3O_8 dissolutions. The most concentrated direct dissolution sample solution made thus far was 300 mg U_3O_8 in 0.1M HTFSI, which equates to 50 mM U. This, however, does not necessarily represent the ultimate solubility of uranium oxide in the ionic liquid.

d. Electrodeposition for targets

The specially designed Teflon cell (Figure 3) had been designed by John Kinyanjui to be used for deposition of targets. The circular deposition area inside had an area of 9.23 cm². In that cell, a sheet of metal acts as the working electrode and surface of deposit, the counter electrode is a Pt disc electrode (1.6 mm diameter), and a reference electrode filled with 0.1 M $AgNO_3$ dissolved in the Me₃NBuTFSI with Ag wire and a Vycor frit. Electrochemistry was performed using a CH Instruments 760b potentiostat under inert atmosphere in an MBraun glovebox.

One of the primary solutions from which deposition was occurring was the 2.01 mM U_3O_8 with 3.25 M HTFSI in Me₃NBuTFSI (the original dissolution solution). The deposits were made by using cyclic voltammetry in the negative potential in an attempt to nucleate the surface followed by a constant negative potential, often for 24 hours and sometimes followed by more time. Using the designed electrodeposition cell for foils eleven deposits were attempted on 316 stainless steel, one was attempted on a sheet of Au mica, and one was attempted on Au foil.

Scanning electron microscopy (SEM) and energy-dispersive x-ray emission spectroscopy (EDX) were completed directly on select electrodeposited samples. SEM images and EDX measurements were taken on a JEOL-5610 scanning electron microscope. The SEM was operating at an accelerating voltage of 20 keV in backscatter mode and an operating distance of 20 mm for the purposes of EDS. Deposits on Au foil collected during previous electrochemistry using the traditional electrochemistry vessel was analyzed by SEM and EDS. The first deposit attempt on stainless steel (designated "SS-A") for targets also had a section taken for SEM and EDS analysis.

Figure 3. Electrochemical cell made of Teflon and designed by John Kinyanjui for electrodeposition attempts for targets

Results and Discussion

a. Karl-Fischer analysis of [Me$_3$NBu][TFSI] samples

The Karl-Fischer analysis of the RTIL [Me$_3$NBu][TFSI] (Table 1) indicates that it can contain as little as 274 ± 2 ppm H_2O, but the RTIL also absorbs some level of water from the atmosphere as well. Each step of the dissolution of 50.1 mg U_3O_8 into]Me$_3$NBu][TFSI] had an aliquot taken and analyzed for water content. The table indicates that some water is introduced under benchtop conditions at each step including the addition of HTFSI, ozone of solution, and dissolution. As a result, the final water content following dissolution is much higher than the baseline contribution in the ionic liquid.

Table 1. Karl-Fischer analysis of H_2O content during steps of the U_3O_8 dissolution process in [Me$_3$NBu][TFSI]

[Me$_3$NBu][TFSI]	% water	Mean	ST DEV	% RSD
1	0.0276			
2	0.0273			
3	0.0274	0.0274	0.0002	0.557%
0.03 M HTFSI in [Me$_3$NBu][TFSI] (bkgd)				
1	0.0365			
2	0.0362			
3	0.0376	0.0368	0.0007	2.005%
0.03 M HTFSI in[Me$_3$NBu][TFSI] (bkgd) - ozone 24 hrs				
1	0.1063			
2	0.0992			
3	0.0973	0.1009	0.0034	3.323%
0.0501 g U$_3$O$_8$ dissolved				
1	0.2016			
2	0.1992			
3	0.2024	0.2011	0.0012	0.586%

After performing a contact experiment on equivalent amounts of the [Me$_3$NBu][TFSI] and ultra pure water and equilibrium was established, the maximum dissolved water in the RTIL portion was analyzed to be $12,060 \pm 1437$ ppm H_2O (Table 2). This would suggest that even if water is absorbed from the atmosphere or produced during the direct dissolution of an actinide oxide, the H_2O content may reach a maximum of $12,060 \pm 1437$ ppm, after which a separate aqueous phase would form. Interestingly, purging a solution with an inert gas such as argon for 24 hours helps to remove excess dissolved water in the RTIL reducing the levels back down towards the baseline water content or lower.

Table 2. Karl-Fischer analysis of H_2O content of the ionic liquid [Me$_3$NBu][TFSI] equilibrium after contact with an equivalent volume of water, followed by purging with inert gas for 24 hours.

water contacted RTIL portion- Week 1	% water	Mean	ST DEV	% RSD
1	1.0419			
2	1.2670			
3	1.3092	1.2060	0.1437	11.915%
water contacted RTIL portion- Week 4				
1	1.1438			
2	1.1921			
3	1.2511	1.1957	0.0537	4.494%
water contacted RTIL portion- Week 4 (argon purged 24 hrs)				
1	0.0075			
2	0.0066			
3	0.0073	0.0071	0.0005	6.625%

Other methods to reduce water content of ionic liquid were investigated to determine how effective each could be and then the best options could be employed to reduce the water content of solutions after dissolution and before electrodepositions were attempted. This was explored after noticing differences initially in obtaining dissolution and then also differences in the successfulness of the resulting deposits from solutions. It was then that it was theorized the water content was different and was not being accounted for in each of the dissolution samples. The results of ionic liquid before and samples after being purged, in contact with molecular sieves or sodium metal is presented below. In general, purging with the nitrogen did not seem to reduce the water content of the ionic liquid below the baseline level. But standard gas has a few hundred ppm of water content, and a drying column was not used in the feed gas but was purchased after this study. The sodium metal did not prove much more successful. The molecular sieves, however, did successfully reduce the water content below the baseline to 200 ± 6 ppm H_2O.

Table 3. Karl-Fischer analysis of H_2O content of the ionic liquid $[Me_3NBu][TFSI]$ with different drying techniques used.

0.1% water standards	% water	Mean	ST DEV	% RSD
1	0.0992			
2	0.1017			
3	0.1063	0.1024	0.0036	3.512%
Me₃NBuTFSI				
1	0.0420			
2	0.0394			
3	0.0411	0.0408	0.0013	3.198%
Me₃NBuTFSI 24 hrs N₂ purge				
1	0.045			
2	0.040			
3	0.040	0.0416	0.0020	4.722%
Me₃NBuTFSI and molecular sieves				
1	0.020833			
2	0.0191			
3	0.0199	0.0200	0.0006	3.002%
Me₃NBuTFSI and Na(m)				
1	0.0496			
2	0.0464			
3	0.0472	0.0477	0.0012	2.488%

b. Preparation of U_3O_8

The synthesis of U_3O_8 with about 0.04% [233]U was completed and a grey solid with a slight green hue to it was the result. A small sample was taken and placed on a holder for powder XRD analysis. The results are featured in Figure 4 where the TOPAS software determined a fit of the sample spectrum to the U_3O_8 C2mm type (also commonly referred to as α-U_3O_8) at 100%. This served to confirm that the U_3O_8 was indeed the result of the synthesis. The procedure used to obtain this product was followed whenever more U_3O_8 was needed for dissolution and electrochemical studies in the RTIL, and a sample of each batch of product was confirmed in this manner by powder XRD after synthesis.
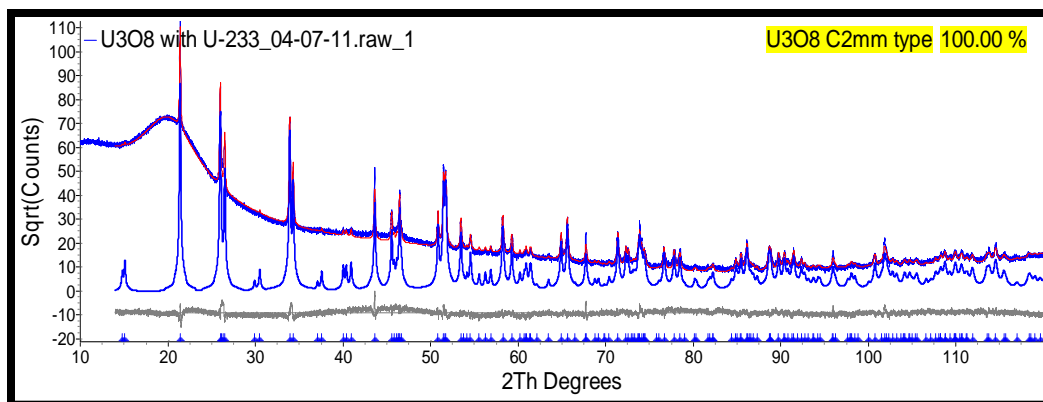
Figure 4. Powder XRD results indicating the prepared product is α-U_3O_8

c. Direct dissolution of U_3O_8 into [Me$_3$NBu][TFSI]

The original dissolution solution was 45 mg U_3O_8 (nat) with 3.27 M HTFSI in [Me$_3$NBu][TFSI]. The sample was stirred and purged with argon for weeks with no apparent change. Once the idea of bubbling with ozone was set up and implemented, the solid dissolved within 24 hours. This original dissolution solution was later used as one of the main sample solutions from which electrodeposition was attempted.

Over time other dissolutions of U_3O_8 were examined including a sample which pre-conditioned the RTIL before adding the U_3O_8 and then underwent sequential ~50 mg U_3O_8 dissolutions. The process is pictured below in Figure 5.

Figure 5. The RTIL before adding U_3O_8 (left), after the addition of U_3O_8 (middle), and after dissolution is complete (right)

The resulting dissolution sample solutions appeared a slight translucent yellow, which was an indication of the dissolved species being uranyl (UO_2^{2+}). This was confirmed when some of the original dissolution sample was sent for extended X-ray absorption fine structure (EXAFS) analysis at the Advanced Photon Source at Argonne National Laboratory. The resulting fitted experimental spectra to that of a uranyl standard is featured in Figure 6. The EXAFS data found uranium to be coordinated to two oxygens at 1.75 Å and another 6 ± 1 oxygens at 2.38 Å. This suggests the shortest bond (1.75 Å) are representative of double bonded oxygens, which supports the dissolved species as being uranyl.[43] The other coordinated oxygens could be from either water or the anion (N(SO$_2$CF$_3$)$_2$) through the sulfonyl oxygens.
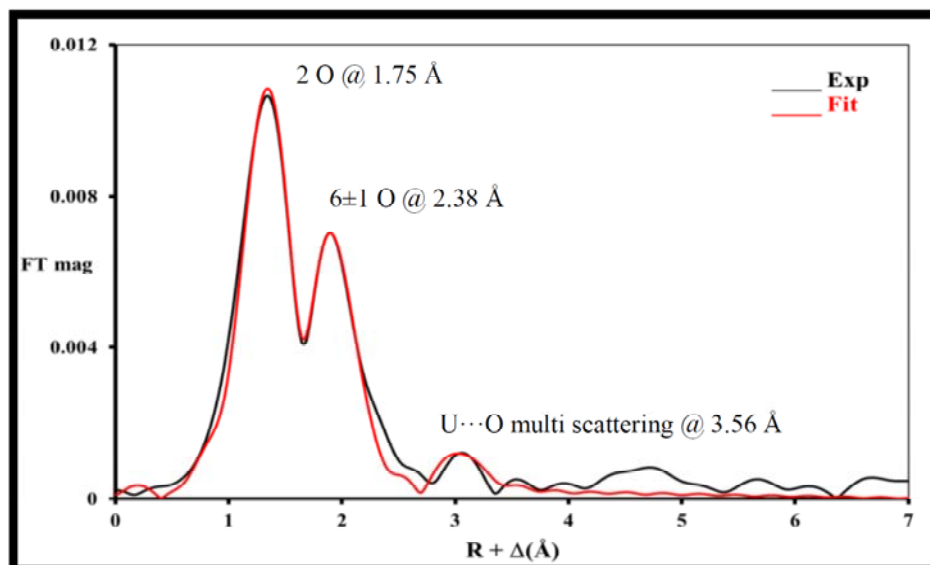
Figure 6. EXAFS analysis revealing the dissolved species to be UO_2^{2+}

UV-Vis absorbance of a sample in which the U_3O_8 was incrementally dissolved into the [Me₃NBu][TFSI] (Figure 7) exhibits multi-peak fine structure centered about 425 nm, which further supports evidence that the dissolved species is uranyl.[44, 45, 46, 47, 48] This dissolution sample was ~300 mg U_3O_8 (50 mM U) into 0.1 M HTFSI in [Me₃NBu][TFSI] and is the most U_3O_8 that has been directly dissolved thus far. However, the maximum solubility likely is greater.
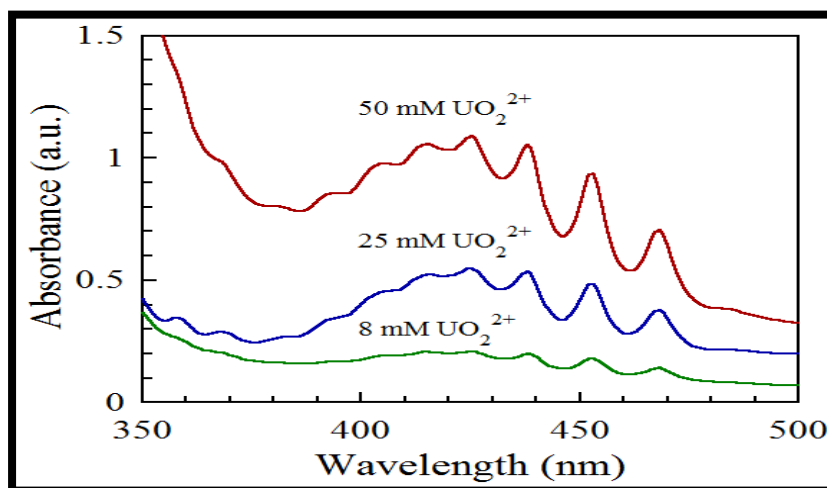
Figure 7. UV-Vis spectra of sequential dissolution of U_3O_8 into [Me₃NBu][TFSI] with 0.1 M HTFSI displaying the fine structure confirming the presence of uranyl (UO_2^{2+})

d. Electrodeposition for targets

A number of electrodepositions from various U_3O_8 dissolution sample solutions were attempted. What follows are some examples and the more noteworthy results of these studies. An example of the possibility of deposition from these direct dissolution [Me₃NBu][TFSI] solutions was the deposition on Au foil from the original U_3O_8 dissolution solution was done

for 48 hours at -2.2 V. A very visible dark grey deposit covered the surface exposed to deposition. The SEM images below in Figure 8 show the magnification and morphology of the deposit at x35 and x1000. EDS (Figure 9) did confirm uranium and oxygen to be present, suggesting the deposits to be a form of uranium oxide. The carbon and fluorine could be in the spectra from residual ionic liquid on the surface. The small amounts of aluminum, silicon, and sodium contaminants origins are yet to be determined.
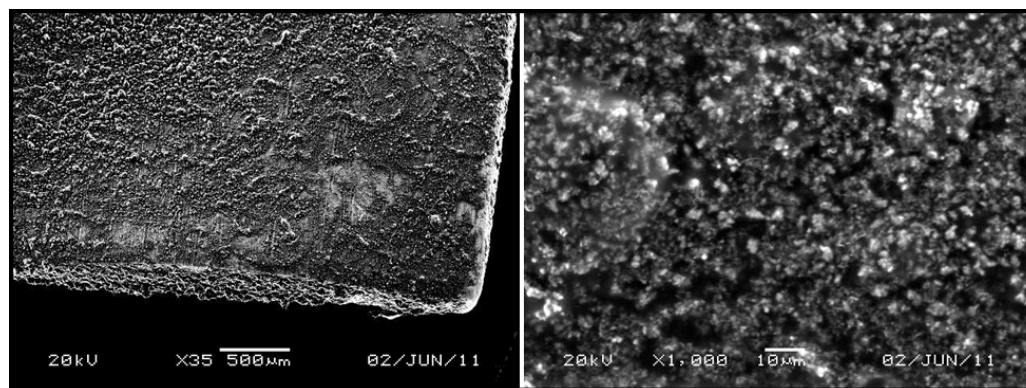
Figure 8. SEM images of the deposits on Au foil from the original U_3O_8 in $Me_3NBuTFSI$ dissolution solution.
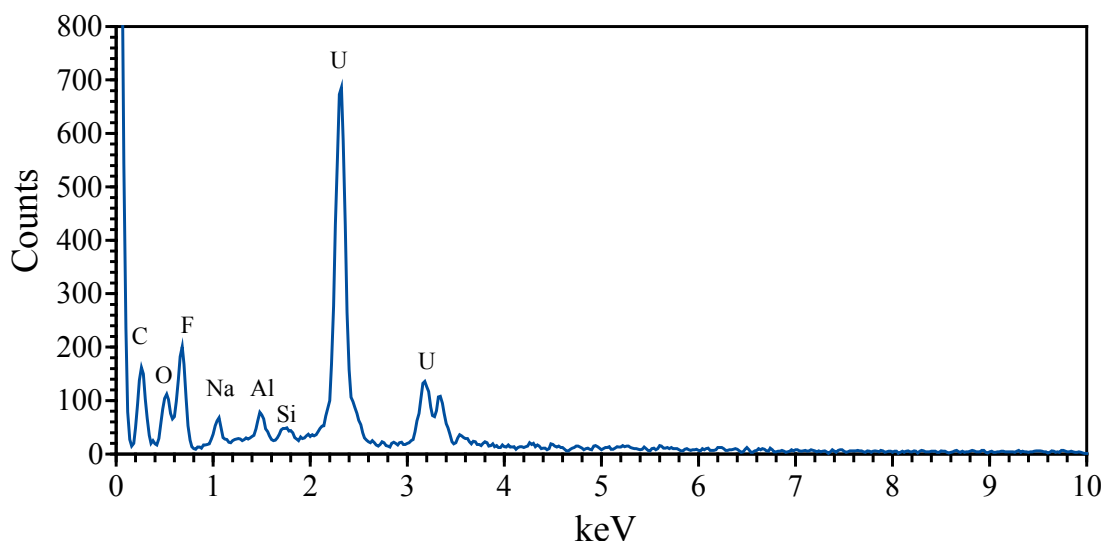
Figure 9. EDS of representative deposit area on Au foil from the original U_3O_8 in $Me_3NBuTFSI$ dissolution solution.

The initial attempt to deposit using the new electrodeposition cell was done with a sheet of 316 stainless steel. This sample was to as "SS-A". The surface was nucleated by running cyclic voltammetry in the window of 1.9 to -2.4 V at 50 mV/s for 200 segments. The resulting CV is below in Figure 10. It seems that perhaps the geometry of the cell causes a high and noisy current response in the more negative region, which was not seen when cyclic voltammetry was ran of the same sample solution in a standard 3-electrode vessel.
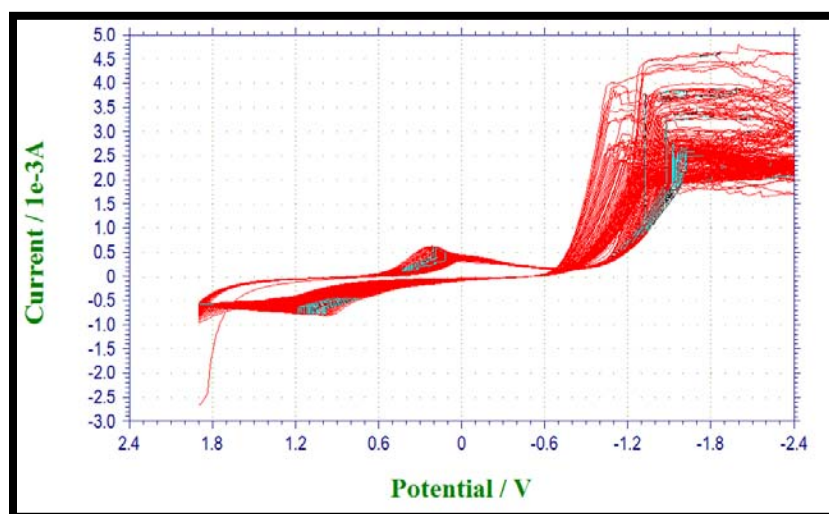
Figure 10. The cyclic voltammetry that was used to nucleate the surface of SS-A for electrodeposition

The constant potential is presented in Figure 11 for SS-A. There were numerous and somewhat regular inreases in the current during deposition. Again, this may be due to geometries of the electrodeposition cell as usually these spikes do not occur in constant potential deposition.
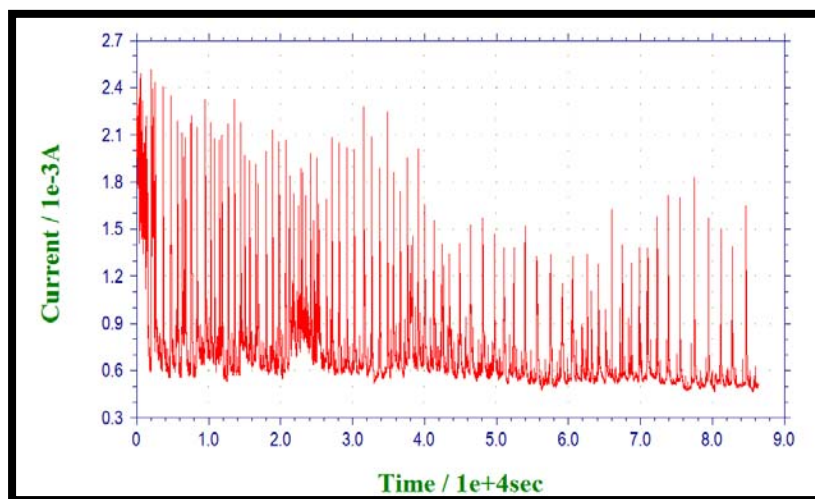

Figure 11. The electro-deposition at constant potential of -2.2 V for SS-A

Figure 12 is a picture of the SS-A deposit, which was visible and brown/grey in nature. While visible deposits such as the one pictured occurred a number of times on the stainless steel, the deposits were not well adhered to the surface. This created a complication when attempting to clean and remove the excess RTIL sample solution from the deposit. Eventually, a procedure to try to clean off this excess RTIL solution was developed: use a heat gun for a few minutes over the deposit area, gently rinse surface with ethanol a few times, use a kim wipe to wipe off the back of the metal and undeposited perimeter of the deposit, allow to dry before determining a post-deposition mass.
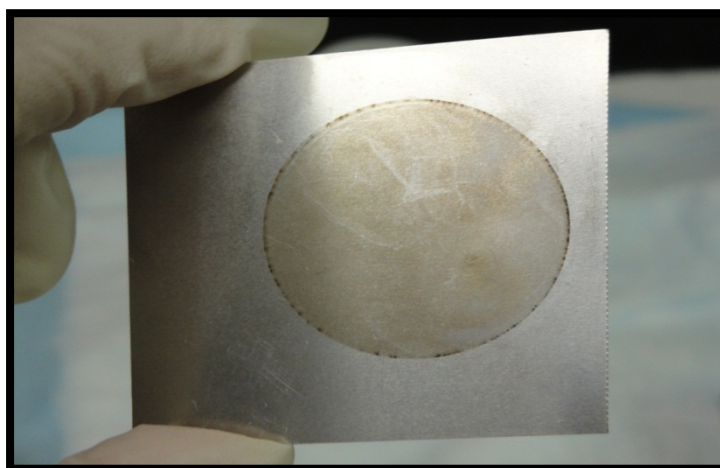

Figure 12. Picture of the deposit SS-A following electrodeposition.

The SS-A deposit was also investigated on SEM. Images in Figure 13 show the deposit boundary on a clipping taken from the SS-A sheet following deposition. The deposit features a light layer of deposit with further developed beads of deposit on the surface. Figure 14 has images of EDS mapping performed on the x1000 magnification SEM sample location showed that uranium was indeed present and in some areas forming beads of deposit but that the prominent feature in the SEM image was in fact comprised of sulfur and perhaps a sulfur salt. Also present in the mapping was an even coverage of oxygen, supporting that a uranium oxide is the major component of the deposit. The sulfur is likely a result of some residual [Me$_3$NBu][TFSI] on the surface of the deposit.
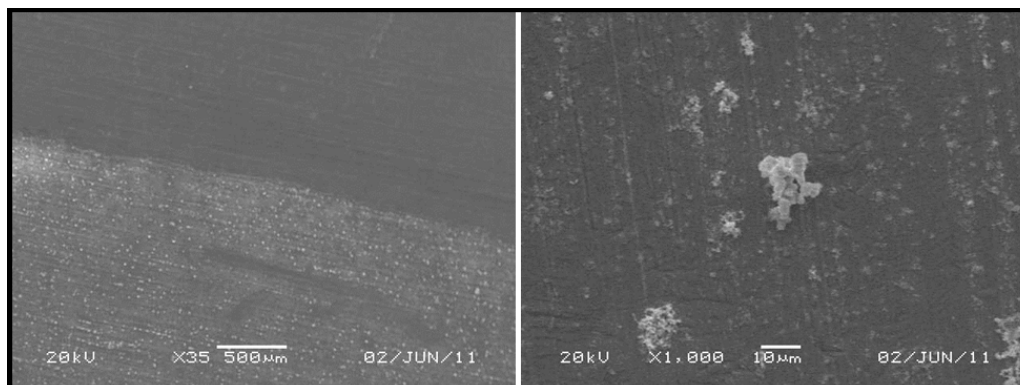

Figure 13. SEM images of deposits on SS-A at x35 and x1000 magnification
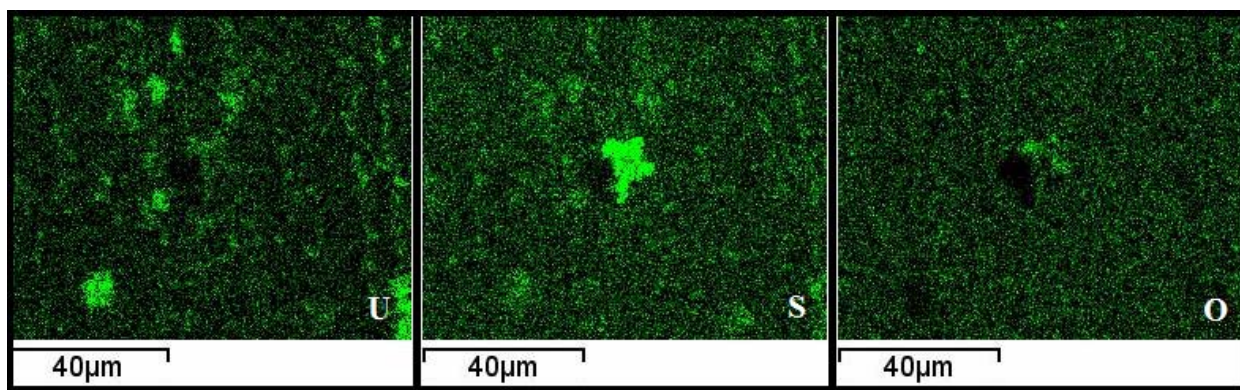
Figure 14. EDS mapping of uranium (left), sulfur (middle), and oxygen (right) of the x1000 magnification of the SS-A deposit

To underscore that the exact chemistry of the direct dissolution and that which occurs after dissolution is not fully known, it was observed that over the course of months the dissolution solutions turned a darker color. It was experienced that newly dissolved sample solutions were not as successful as the older dissolution sample solutions (such as the original 2.12 mM U with 3.27 M HTFSI in [Me$_3$NBu][TFSI]). In fact, when electrodeposition was attempted from the more newly dissolved sample solutions of similar uranium concentration to the original dissolution solution (2 mM up to 10 mM U with 0.1 M HTFSI in [Me$_3$NBu][TFSI]), only some light yellow precipitate was found to form on the counter electrode and some spots on the stainless steel deposition surface. It was also noticed that over time a solution of RTIL with just HTFSI added to it also colors over time from clear to a slight yellowed color. At this point, the explanation to these observances is unknown. Therefore, it is apparent that a deeper understanding of the chemistry occurring in the dissolution samples is necessary and may further develop the efficiency of producing electrodeposits for targets.

Conclusion

The goal of the project was to produce electrodeposited targets of ~1 mg/cm^2 from the directly dissolved U$_3$O$_8$ [Me$_3$NBu][TFSI] sample solutions. This would allow, should deposits be free from unwanted contamination which may interfere, for neutron activation studies of the electrodeposited uDU target. The estimated deposit density which would be ideal before too much alpha attenuation was occurring was on the order of the 1 mg/cm^2. The deposit densities that were achieved were up to 0.6 mg/cm^2 in the case of target foils. The deposit from solution on a small piece of Au foil did observe a much thicker deposit, but the area of deposit was also smaller. Since the desired deposit density of 1 mg/cm^2 has not yet been achieved, the uDU that Dr. Beller obtained was not yet used in these studies as there was limited uDU material. It may be that attention to reduce the water content of the ionic liquid after dissolution could help to improve the electrodeposition as well as the smaller Teflon cell with a diameter on par with the eventual neutron beam for neutron activation studies. Eventually, for larger foil areas a more powerful potentiostat would be required.

Accomplishments supported by this research include the proof of principle and multiple subsequent successful dissolutions of U_3O_8 into [Me₃NBu][TFSI] and precedented the ability to also extend this concept to other f-element oxides. Also, it was shown that from this RTIL solution a uranium oxide can be electrodeposited onto Au foil and 316 stainless steel. There is a possibility that efforts to substantially remove water resulting in a "dry" RTIL after dissolution may even provide deposits of uranium or other actinide metal.

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